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III.

THERMO-ELECTRICITY. — PELTIER AND THOMSON EFFECTS.

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Presented by Professor Trowbridge, June 8, 1881.

THERE are two theories regarding the cause of the thermo-electric current. That held by Le Roux, Clausius, and most French physicists is that the heat effects which cause the current take place only at the junctions. The theory held by Sir William Thomson, Tait, and Maxwell is that the heat effects which cause the current take place, not only at the junctions, but along the metals themselves.

Let π and π^1 denote the heat — measured in dynamical equivalents — absorbed and evolved at the hot and cold junctions respectively in unit time by unit current. Let E be the electromotive force of a battery, maintaining a current I in such a direction as to cause absorption of heat at the hot junction. Then if R be the whole resistance of the circuit, we have by Joule's law and the first law of thermodynamics: —

$$EI + \pi I - \pi_1 I = RI^2. \tag{1}$$

Supposing the whole energy of the current wasted in heat. Also: —

$$I = \frac{E + \pi - \pi'}{R} \tag{2}$$

It appears, then, that, owing to the excess of the absorption of heat at the hot junction over the evolution at the cold junction, there arises an electromotive force $\pi - \pi_1$ helping to drive the current in the direction giving heat absorption at the hot junction. We may suppose, and shall henceforth suppose, that $E = O$, and then the current will be maintained entirely by the electromotive force $\pi - \pi_1$.

Now, apply the second law of thermodynamics. "The application of the second law is of a more hypothetical character. Still it seems a reasonable hypothesis to assume that the Peltier effects, and other heat effects, if any, which vary as the first power of the current strength, taken by themselves, are subject to the second law of thermodynamics."

This law gives : —

$$\frac{\pi I}{\theta} - \frac{\pi' I}{\theta'} = 0$$

θ and θ^1 being the absolute temperatures of the hot and cold junctions.

$$\therefore \frac{\pi}{\theta} = \frac{\pi'}{\theta'} \tag{3}$$

$$\therefore \pi = C\theta$$

C being a constant, depending only on the nature of the metals.

In accordance with this, the electromotive force in the circuit $= C(\theta - \theta_1)$ $\therefore$ it would be proportional to the difference between the temperatures of the junctions.

"Now, this conclusion is wholly inconsistent with the existence of thermo-electric inversion. We must, therefore, either deny the applicability of the second law, or else seek for reversible heat effects other than those of Peltier." This was essentially the reasoning that led Thomson to the discovery of the Thomson effect. Before questioning Thomson's conclusion, it is best to consider the formulæ which are deduced from his hypothesis.

Suppose we have a circuit of two metals. Let the heat absorbed by the Thomson effect in passing from a point at temperature θ to a point at temperature $\theta + d\theta$ in one metal be $\sigma_1 d\theta$ per unit current per unit time. Let $\sigma_2 d\theta$ be the corresponding expression for the other metal. σ_1 and σ_2 are functions of the temperature. They depend on the nature of the metals, but are independent of the form or magnitude of the section of the conductors. These effects are proportional to the first power of the current strength.

By the first law of thermodynamics : —

$$EI + \pi I - \pi' I + I\int_{\theta'}^{\theta} (\sigma_1 - \sigma_2)\, d\theta = RI^2 \tag{α}$$

$$\therefore I = \frac{E + \pi - \pi' + \int_{\theta'}^{\theta} (\sigma_1 - \sigma_2)\, d\theta}{R} \tag{β}$$

If $E = O$ we have as the electromotive force of the thermo-electric current, by the same reasoning as before : —

$$e = \pi - \pi' + \int_{\theta'}^{\theta} (\sigma_1 - \sigma_2)\, d\theta \tag{γ}$$

The second law of thermodynamics gives: —

$$o = \frac{\pi}{\theta} - \frac{\pi'}{\theta'} + \int_{\theta'}^{\theta} \left(\frac{\sigma_1 - \sigma_2}{\theta}\right) d\theta \qquad (\delta)$$

Differentiate (δ)

$$\frac{d}{d\theta}\left(\frac{\pi}{\theta}\right) + \frac{\sigma_1 - \sigma_2}{\theta} = 0 \qquad (\eta)$$

$$\therefore \frac{\sigma_1 - \sigma_2}{\theta} = -\frac{d}{d\theta}\left(\frac{\pi}{\theta}\right)$$

performing the differentiation

$$= \frac{\theta \frac{d\pi}{d\theta} - \pi}{\theta^2}$$

$$\therefore \sigma_1 - \sigma_2 = -\frac{d\pi}{d\theta} + \frac{\pi}{\theta}$$

Substitute in (γ)

$$e = \pi - \pi' - \int_{\theta'}^{\theta} \left(\frac{d\pi}{d\theta} - \frac{\pi}{\theta}\right) d\theta$$

$$= \pi - \pi' - (\pi - \pi') + \int_{\theta'}^{\theta} \frac{\pi}{\theta}\, d\theta$$

$$\therefore e = \int_{\theta'}^{\theta} \frac{\pi}{\theta}\, d\theta \qquad (\xi)$$

or

$$e = -\int\!\!\int \frac{\sigma_1 - \sigma_2}{\theta} \qquad (\omega)$$

from (η).

If, as Tait supposes, σ is proportional to the first power of the absolute temperature, $\sigma = k\theta$ equation (w) becomes: —

$$e = -\left[k\theta^2 + k'\theta + k''\right]$$

$\therefore$ the thermo-electric curve is a parabola.

The basis of all the preceding is taken from the British Encyclopædia. Maxwell's demonstration is essentially the same. (§§ 249–251, Vol. I., Maxwell's Electricity and Magnetism.)

When no current was passing from an external battery eq. (2) became

$$I = \frac{\pi - \pi'}{R}$$

Let

$$\pi - \pi' = \mathfrak{E} \qquad \therefore I = \frac{\mathfrak{E}}{R}$$

In other words, it was said that the heat $\circlearrowright$ — the amount of heat absorbed in unit time by unit current in crossing the hot junction exceeding that evolved at the cold junction — was sufficient to produce a current of strength I.

Now, when a current from an outside source is passed through the circuit in the same direction as I, an amount of heat $\circlearrowright C$ disappears, — C being the strength of the external current: what becomes of this heat? A certain amount of energy disappears: what is its equivalent?

If the heat $\circlearrowright$ is sufficient to produce a current of strength I, the heat $\circlearrowright C$ is great enough to produce a current C times as strong as I $\therefore$ a current of strength CI.

When the current C is passing through the circuit we should then expect to find it increased (or decreased) by a current CI — the equivalent of the amount of heat absorbed by C. Thus, when an external current passes through a thermo-electric element, we should expect to have as the total current in the circuit, $C+I\pm CI$; that is, the resultant current should be much greater (or much less) than $C+I$.

But, in several experiments that were made, it was observed that the resultant current always equalled exactly $C+I$.

Now, if the Peltier effect is the cause of the thermo-electric current, enough heat has disappeared to create a current C times as strong as the proper thermo-electric current; but experiment shows that the thermo-electric current is perceptible, while this other current is imperceptible. We must, therefore, conclude that this current, which is equivalent to an amount of heat $\circlearrowright C$, is not C times as great as the proper thermo-electric current; and hence the proper thermo-electric current cannot be the equivalent of the amount of heat $\circlearrowright$. In other words, the Peltier effect cannot be the cause of the thermo-electric current.

An unsuccessful experiment was made to prove that the Peltier effect was not great enough to be the cause of the thermo-electric current. The failure was due to the fact that the heat absorbed was too small to be measured. The principle of the experiment was as follows: —

Place the thermo-electric junction in a vessel of mercury, after heating the mercury to a certain temperature let it cool, the circuit being broken so that no current passes. From a thermometer placed in the mercury read the temperatures at definite times, and construct a curve, having the temperatures as ordinates, and the corresponding times as abscissas. Next draw a similar curve when the thermo current is passing. Let the current run through a galvanometer, and observe the deflection of the galvanometer every time a reading of the thermometer is taken. This will give a third curve, giving the thermo-electric current at any time, corresponding to any temperature of the second curve. Finally, pass a current of known strength I from an external source through the junction in the direction of the proper thermo current, and get a fourth curve representing the fall of temperature for this case.

The equations of all these curves being known, we can find from the two first the rate at which heat is absorbed by a thermo-electric current of any strength given by the third curve. Let $h =$ the heat absorbed in unit time by this thermo-electric current of strength i. From the first and fourth curves we can find the amount of heat H absorbed in unit time by the battery current I.

Now, if the heat H is merely the heat absorbed by the Peltier effect, we have — as the heat of the Peltier effect is simply proportional to the current strength: —

$$h : H :: i : I. \tag{4}$$

But if, as I supposed, h was much greater than the heat absorbed by the Peltier effect, this equation would not be satisfied.

The thermo element used was of German silver and iron. The hot junction was shaped in the form of a ring and placed in a small vessel of mercury, the bulb of the thermometer being placed in the centre of the ring. The first two curves, however, were identical, though German silver and iron constitute one of the strongest thermo elements. The thermometer fell at exactly the same rate whether the current was passing or not.

We have not, however, considered the Thomson effect. But the same reasoning used in the case of the Peltier effect applies also here.

From equation (γ) it was seen that the proper thermo-electric current was proportional to

$$\pi - \pi' + \int_{\theta'}^{\theta} (\sigma_1 - \sigma_2)\, d\theta$$

Let

$$\int_{\theta'}^{\theta} (\sigma_1 - \sigma_2)\, d\theta = S$$

Then this current is proportional to $\text{໑} + S$. That is, $\text{໑} + S$ is the whole heat absorbed in the circuit by unit current in unit time.

If, now, we pass through the circuit an external current of strength C, the whole heat absorbed is $(\vartheta + S)$ C.

This should be enough heat to produce a current C times as strong as the proper thermo-electric current, *if the thermo-electric current is due to the heat* $\vartheta + S$.

If, then, I be the strength of the thermo-electric current, we should expect that the whole current in the circuit would be:—

$$C + I \pm CI.$$

But experiment shows that the whole current exactly $= C + I$. We must, then, conclude that the current which is equivalent to the heat $(\vartheta + S)\ C$ is not C times as great as the proper thermo-electric current; consequently, the thermo-electric current cannot be the equivalent of the heat $\vartheta + S$. In other words, the thermo-electric current cannot be the equivalent of the Thomson and Peltier effects.

All the experiments that have been made on the Peltier and Thomson effects have been made when these phenomena appeared as the result of a current, not when they appeared as its cause. The heat absorbed by a thermo-electric current itself has never been measured. All measurements of the heat effects have been made by passing an outside current through the circuit, the heat effects due to the thermo-electric current itself being too small to be measured. But we have no right to suppose, *à priori*, that at the hot junction of a thermo element the only heat absorbed in the production of the thermo-electric current is that due to the Peltier effect. If, in the experiment that I attempted, h had satisfied equation (4), then the heat due to the Peltier effect would have been the only heat absorbed at the hot junction by the thermo-electric current. But, as the experiment was a failure, there are no grounds for this assumption. It is, therefore, not surprising that equations (1), (2), and (3), which are based on the assumption that the Peltier effect is the only heat effect at the hot junction which causes the thermo-electric current, should give results inconsistent with experiment.

The Thomson effect, even more than the Peltier effect, appears to be the result of a current, not the cause.

All experiments on the Thomson effect are made by passing a strong current along a bar of metal, the ends of which are at different temperatures. It is then found that the temperatures of fixed points on the bar are different when the current is passing from what they were before it passed. In some metals the temperature is raised, in others diminished, as the current passes from the hot to the cold end of the bar. Thomson attributed this to the fact that in some metals the current evolved heat in passing from hot to cold parts; in others it absorbed heat. And the difference between the heat absorbed in one metal, and that evolved in the other, he supposed to be one cause of the thermo-electric current.

Another explanation is that the current of electricity changes the thermal conductivity of the bar, in some metals increasing the conductivity, and diminishing it in others.

It is well known that the electric current modifies the physical properties of metals along which it passes. It changes their cohesion, in some cases increasing it, in others diminishing it. The elasticity of metals is also changed under the influence of electricity. What is more probable than that the thermal conductivity should also be changed?

There are many objections to the view taken by Thomson. The numbers expressing the Thomson effect bear no apparent relation to the thermo-electric current; and, moreover, the effect is entirely too small to produce even the weakest thermo-electric current.

The fact that the formulæ deduced on Thomson's hypothesis agree with experimental results is of but little importance. The thermo-electric curves determined experimentally are, approximately, parabolas. Thomson's equation is also that of a parabola. But any theory, based on the supposition that the heat effects are proportional to the current strength, will give the equation of a parabola.

It was mentioned that the current $(\vartheta + S)\ C$ was imperceptible. In the few experiments that were made the current C was very feeble, not much greater than the thermo-electric current I, which was given by an element of German silver and iron. The resistance of the circuit was about two hundred ohms. Consequently, the current equivalent to the extremely small amount of heat $(\vartheta + S)\ C$ might readily have produced no apparent effect.

I have attempted to show that the Peltier and Thomson effects cannot be the whole cause of the thermo-electric current. The true cause is yet to be discovered.

Many unsuccessful attempts have been made to find relations between the strength of the thermo-electric current and the physical properties of the metals of the thermo element. To completely solve the problem, however, we must know the way in which the physical properties of the metals change, when the metals are under the influence of heat and a current of electricity.

The thermo-electric current depends essentially on the differences of the two metals. The slightest change in the structure or the composition of the metals makes a perceptible change in the current. Therefore, to determine the variations of the electric current with the temperature, it is necessary to know the variations of the metals with the temperature. A junction of iron and silver might be expected to give twice as strong a current at 100° as at 50°. This might be the case if the iron and silver were exactly the same at 100° as at 50°; but iron at 100° is a different metal from iron at 50°: the thermal conductivity, the electric conductivity, the specific gravity, and many other properties have changed. It may be due to this fact — that the properties of the metals change with the temperature — that the thermo-electric lines are not straight.